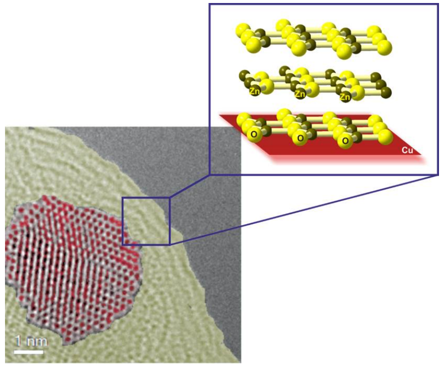
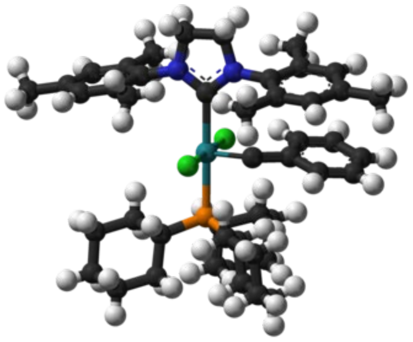
Model Studies in Heterogeneous Catalysis at the Atomic Scale

Hajo Freund (Fritz-Haber-Institut of the MPG)

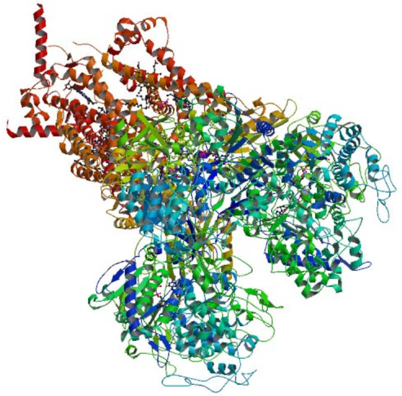
Heterogeneous Catalysis

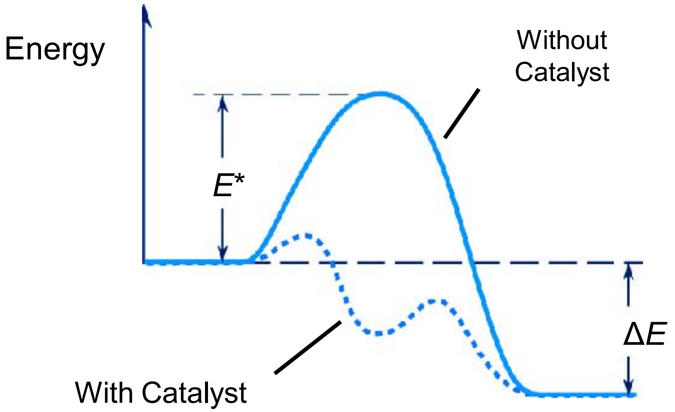


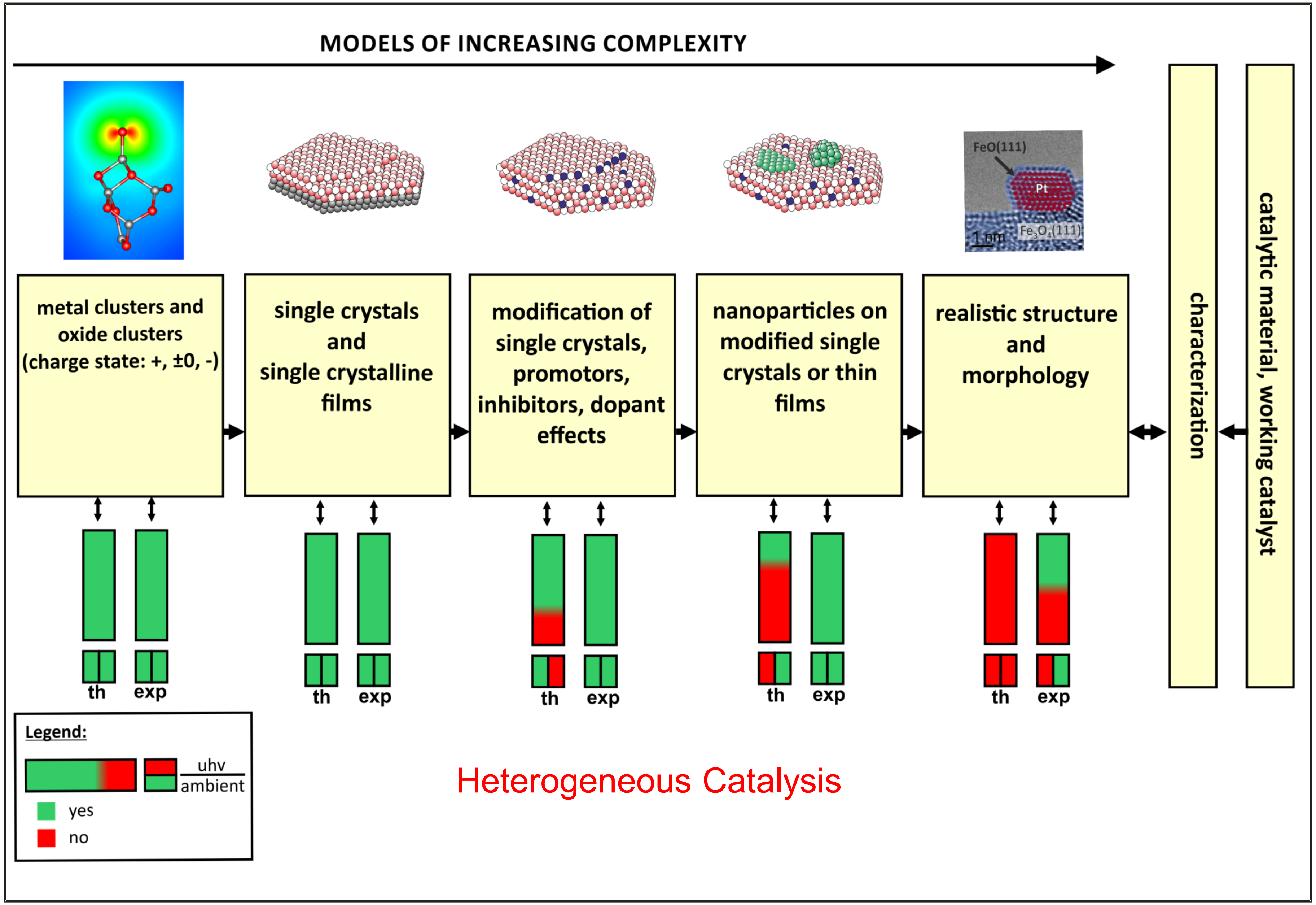
Homogeneous Catalysis



Enzymatic Catalysis



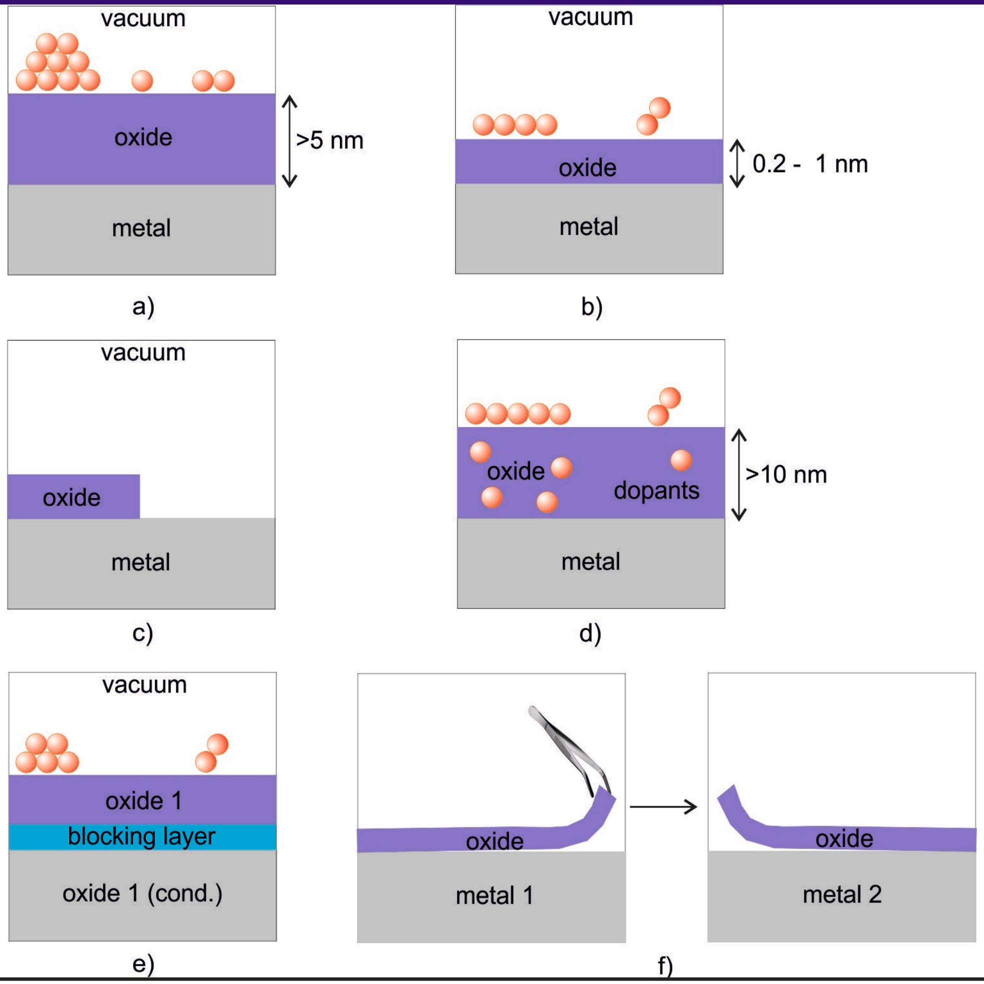




J. Sauer, H.-J. Freund; Catal Lett 145, 109 (2015)

Thin Oxide Film Systems

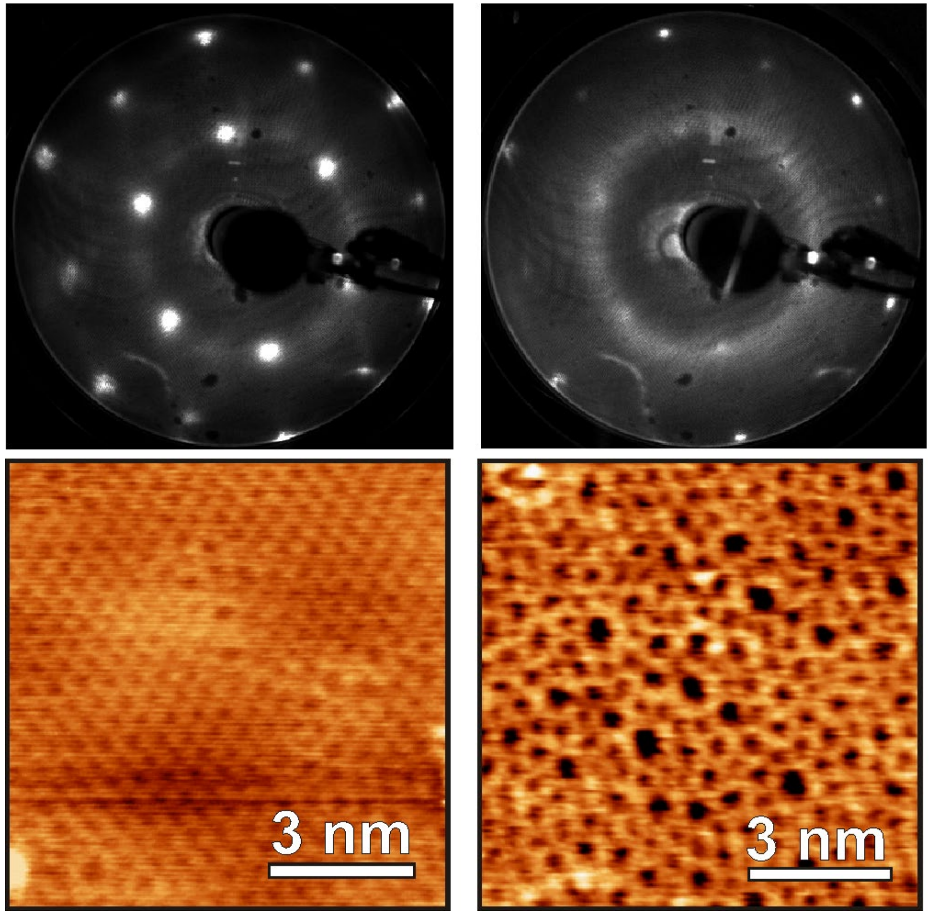
Scenarios



H.-J. Freund; Perspective J. Amer.Chem.Soc. 138, 8985 (2016)

Crystalline and Vitreous Silica Films

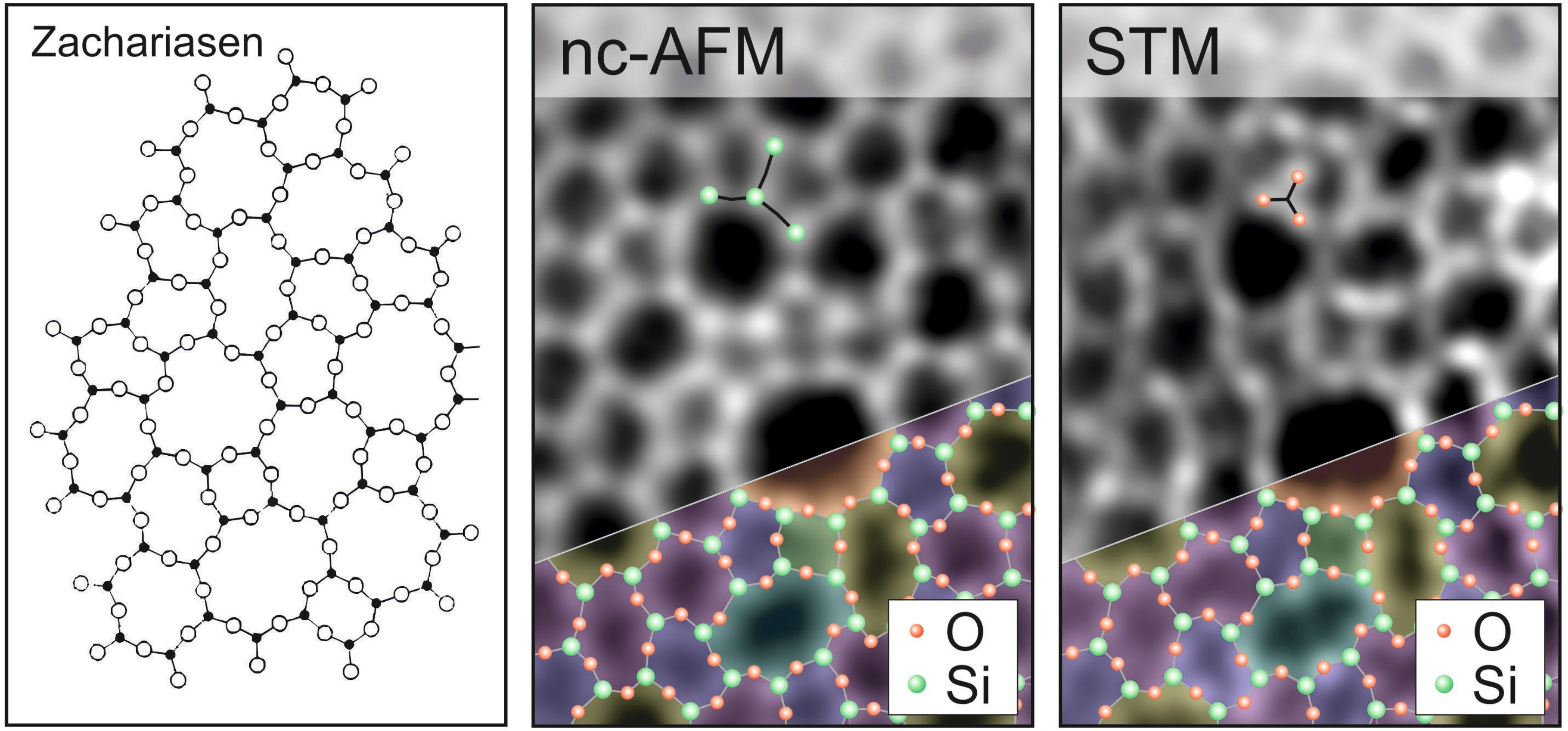
STM and LEED



B. Yang, W.R.Kaden, L.Yu, J.A.Boscoboinik, J.Martynova, L.Lichtenstein,M. Heyde, M.Sterrer, R.Włodarczyk,M. Sierka, J.Sauer, S. Shaikhutdinov, H.-J. Freund PCCP 14, 11344 (2012)

Scanning Probe: nc-AFM vs. STM

Simultaneous Imaging of Si and O



A_{osc} = 0.27 nm, const. height

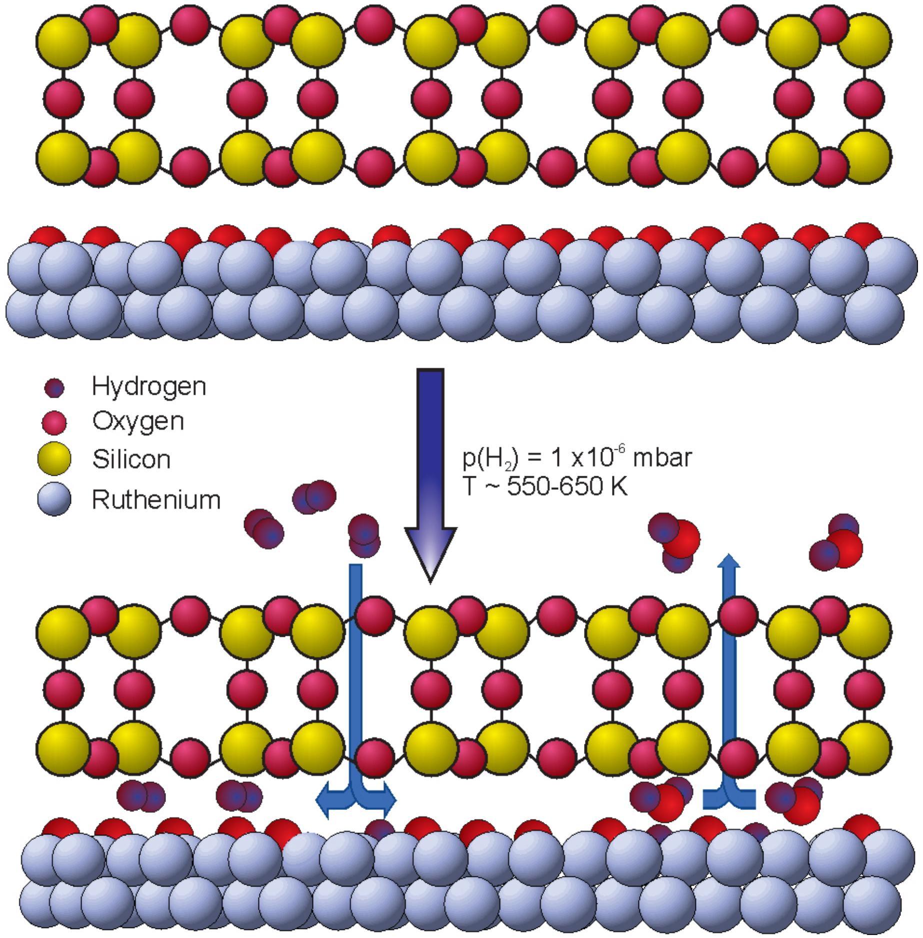
V_S = 0.1 V, const. height

W.H. Zachariasen,
J.Amer.Chem.Soc. 54, 3841(1932)

L. Lichtenstein, M. Heyde, H.-J. Freund, J. Phys. Chem. C 116 (2012) 20426

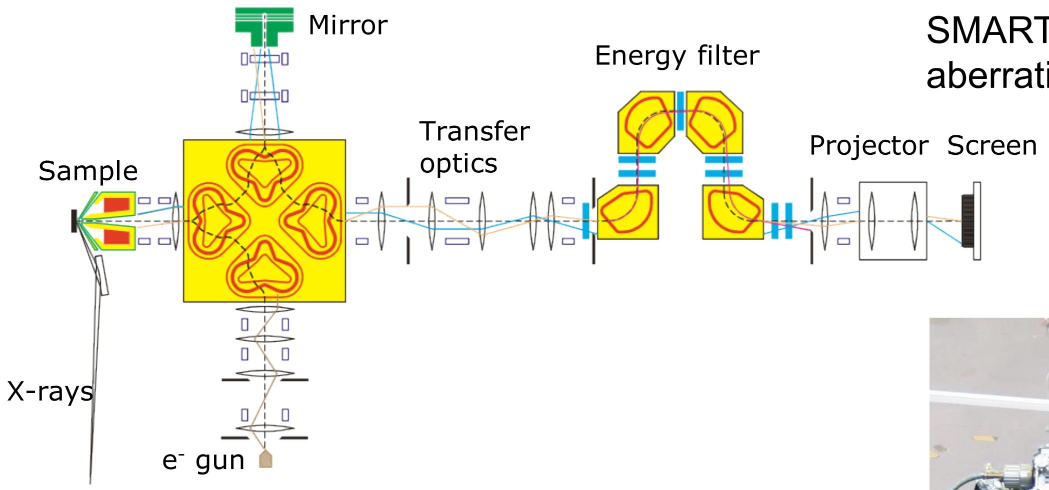
Reactions in Confined Space

Water Formation

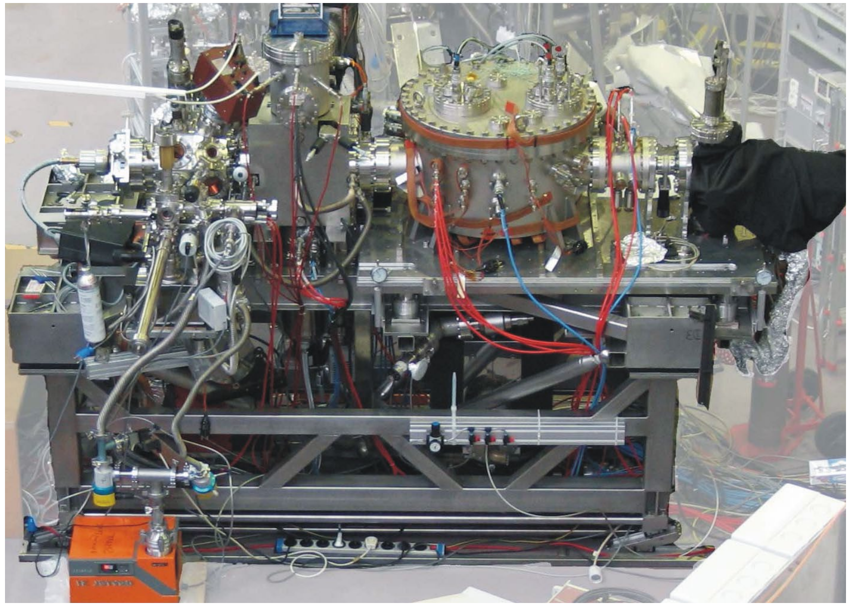


SMART

Experimental Setup



SMART: Spectro-microscope with aberration correction for many relevant techniques



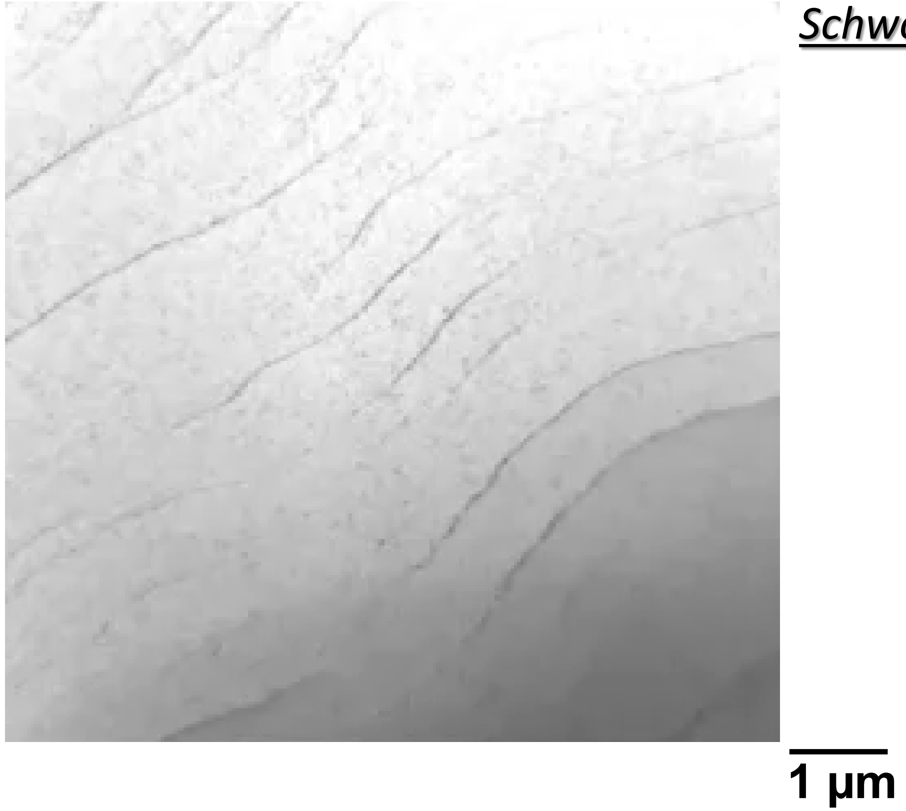
- Energy resolution: 180 meV
- Lateral resolution: 2.6 nm (LEEM), 18 nm (XPEEM)
- Temperature range: 100 ÷ 2000 K;
- Pressure range: 10^{-11} ÷ 10^{-5} mbar;
- Photon range: 80 ÷ 1500 eV
- surface sensitive
- temporal evolution
- multi-method: microscopy-diffraction-spectroscopy

R. Fink et al. J. Elec. Spec. Rel. Phen. 84, 231 (1997)

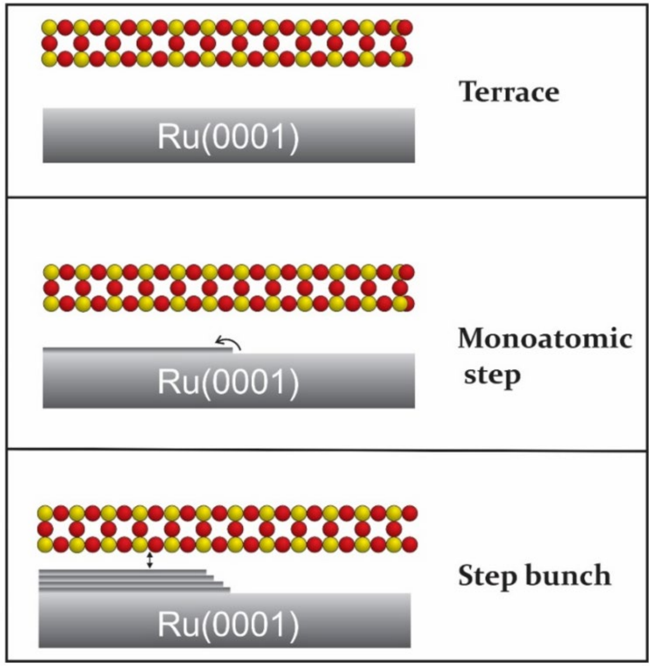
Chemistry in confined space

H_2 intercalation at closed Silica films: *real time* observation

Annealing @ 550 K in $p(H_2) = 1 \times 10^{-6}$ mbar



Schwoebel barrier for diffusion

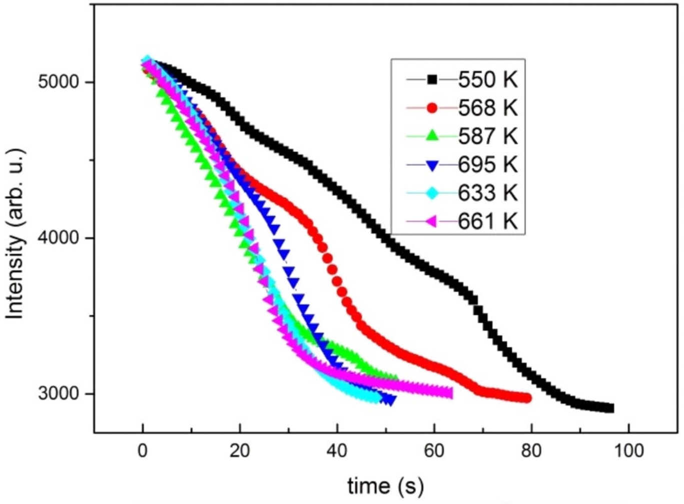


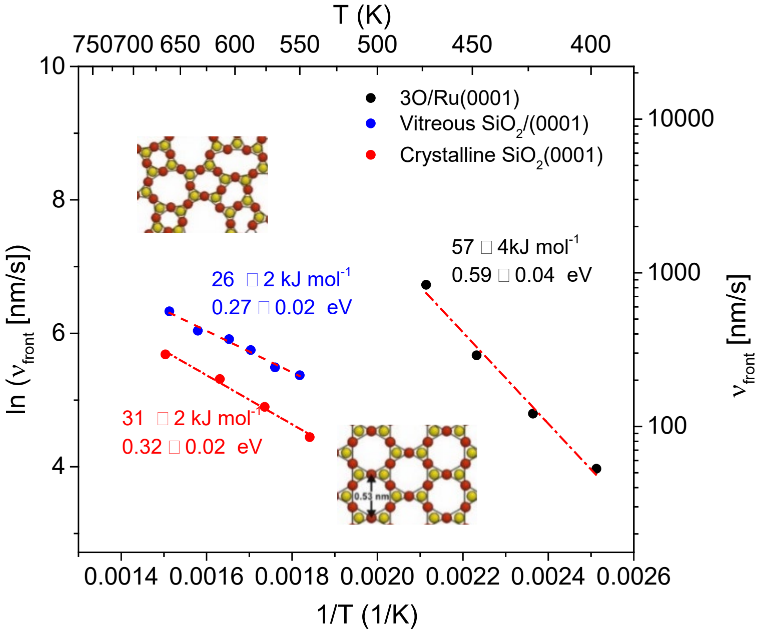
M. J. Prieto, H. W. Klemm, F. Xiong, D. M. Gottlob, D. Menzel, T. Schmidt, HJF Angew. Chem. Int. Ed 57, 8749 (2018)

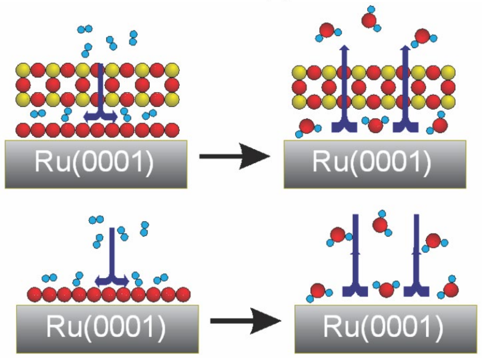
Chemistry in confined space

H_2O formation at closed Silica films: *real time* observation

Activation energy E_a for water reaction







<u>BL Silica/Ru(0001) – confined space</u>:

E_a= 0.27 ± 0.02 – 0.32 ±0.02 eV

<u>Bare Ru(0001)</u>:

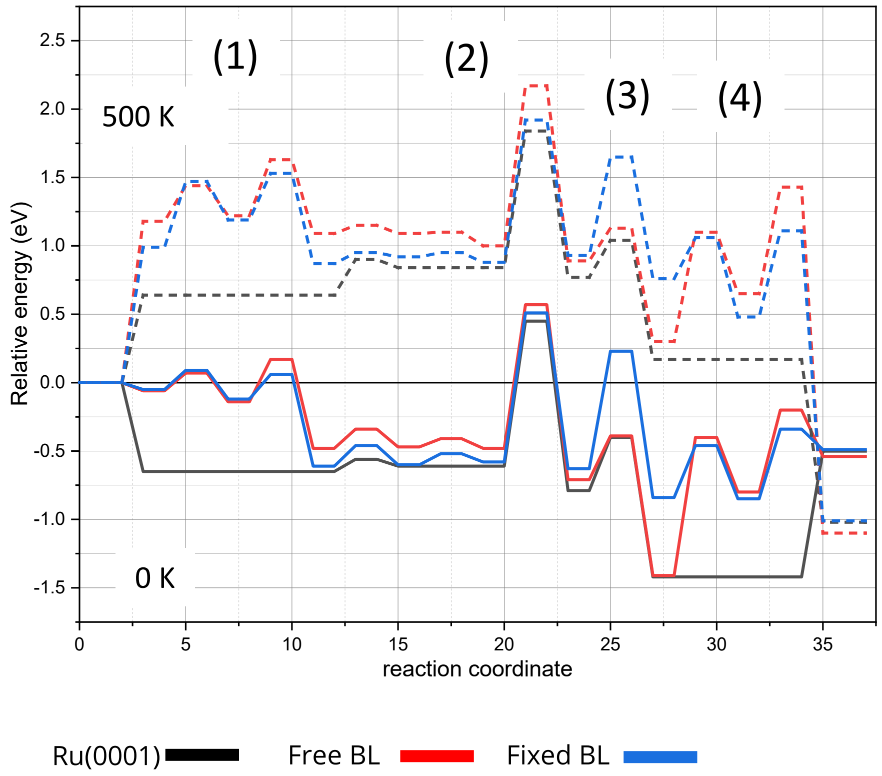
E_a= 0.50 - 0.55 eV

M. Prieto, H. Klemm, F. Xiong, D. Gottlob, D. Menzel, Th. Schmidt, H.-J. Freund; Angew. Chem. Int. Ed. 57, 8749 (2018)

Chemistry in Confined Space

Modelling Elementary Reaction Steps by DFT

Kinetic equations



$$\frac{\partial n_H}{\partial t} = -2k_{-1}n_H^2 + 2k_1 n_*^2 - k_2 n_H n_O - k_3 n_H n_{OH} + D_H \frac{\partial^2 n_H}{\partial x^2}$$

$$\frac{\partial n_O}{\partial t} = -k_2 n_H n_O$$

$$\frac{\partial n_{OH}}{\partial t} = k_2 n_H n_O - k_3 n_H n_{OH}$$

$$\frac{\partial n_{H_2O}}{\partial t} = k_3 n_H n_{OH} - k_4 n_{H_2O}$$

$$n_* = n^0 - n_H - n_O - n_{OH} - n_{H_2O}$$

Max. density of free sites:

$n^0 = n_*^{max} = \frac{3}{A_{cell}}$ = 1.18 10^{19} 1/m^2

$$n_{\mathrm{O}}^{max} = n^0$$

$$n_{\mathrm{H}}^{max} = \alpha\, n^0$$

$$n_{\mathrm{OH}}^{max} = \frac{k_2}{k_3} n^0$$

$$n_{\mathrm{H_2O}}^{max} = \frac{1}{4}\frac{k_2}{k_4}\alpha\, {n^0}^2$$

With $\alpha = \frac{1}{1+\sqrt{\frac{k_{-1}}{k_1}}} \approx \sqrt{\frac{k_1}{k_{-1}}}$

Dr. Denis Usvyat (HU), M.Sc. Thomas Mullan (HU) and Dr. Mark Schlutow (FU)

M. J. Prieto, T. Mullan, M. Schlutow, D. M. Gottlob, L. Tanase, D. Menzel, J. Sauer, D. Usvyat, T. Schmidt, HJF, JACS 143, 8780 (2021)

Thanks

The Department just before it was closed

Chemical Physics Department Workshop, Ringberg, 2018